Photo-induced Reduction of Pyridinium Ions catalysed by Zinc(II) Tetraphenylporphyrin

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Photo-induced (>460 nm) Zn^{II} tetraphenylporphyrin-catalysed reduction of 1,2,6-trimethyl-3,5-bisethoxycarbonylpyridinium perchlorate (1a) and 1-methyl-3-carbamoylpyridinium perchlorate (1b) has been studied. 1,2,6-Trimethyl-1,2-dihydro-3,5-bisethoxycarbonylpyridine (2a), a reduction product, was formed by irradiation of (1a) in an aqueous mixture of ascorbic acid, sodium laurylbenzenesulphonate, polyoxyethylene octylphenyl ether, and Zn^{II} tetraphenylporphyrin, whereas a corresponding 1,2-dihydropyridine (2b) was not obtained from 1-methyl-3-carbamoylpyridinium perchlorate (1b) under similar conditions.

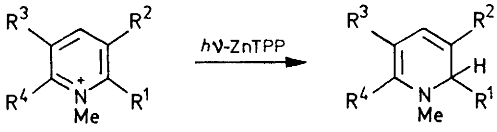
IN recent years, photochemical reactions utilizing visible light have become interesting in relation to the storage of solar energy as chemical energy.[1] Some metalloporphyrins [2] and analogous complexes,[3] upon electronic excitation, either accept an electron from other compounds [3f-h] or transfer one to them.[2,3a-e]

There are few reports that organic compounds are photoreduced by visible light in the presence of metalloporphyrins. Whitten [4] reported that water was decomposed into hydrogen and oxygen using a monolayer assembly system on irradiation. Matsuo [5] has reported the zinc(II) tetraphenylporphyrin (ZnTPP) catalysed photoreduction of sodium anthraquinone-β-sulphonate to the dihydroxyanthracene-β-sulphonate over anionic micelles.

We have observed that a pyridinium ion can be photoreduced to its 1,2-dihydropyridine by visible light in the presence of ZnTPP. By analogy, nicotinamide adenine dinucleotide phosphate (NADP), which has a pyridinium function, was reported to be efficiently converted into its dihydro compound ($NADPH_2$) in photosynthesis of green plants involving chlorophyll.[6]

RESULTS AND DISCUSSION

An aqueous micelle solution of 1,2,6-trimethyl-3,5-bisethoxycarbonylpyridinium perchlorate (1a) (4×10^{-3}M) and the surface active agents sodium laurylbenzenesulphonate (0.005M) and polyoxyethylene octylphenyl ether, $C_8H_{17}C_6H_4O[CH_2CH_2O]_{10}H$, 0.67% (v/v) was irradiated for 4 h by a 150 W halogen lamp. The radiation was passed through a Corning colour filter (3-71) which is transparent at wavelengths >460 nm. The reaction product was shown by high pressure liquid chromatography and t.l.c. to be the corresponding 1,2-dihydropyridine (2a) by comparison with an authentic specimen. The yield of (2a) was low (*ca.* 1%) based on the starting pyridinium ion (1a). No other product from (1a) was detected.



(1)

(1) (2)

a; R^1 = Me, R^2 = R^3 = CO_2Et, R^4 = Me
b; R^1 = H, R^2 = $CONH_2$, R^3 = R^4 = H

No (2a) was obtained at all under other reaction conditions shown in the Table.

Run	Porphyrin	Reducing agent	Solvent	Micelle system
1	Chlorophyll [a]	Ascorbic acid	H_2O	LBS [b]
2	Chlorophyll [a]	EDTA	Propan-2-ol	LBS [b]
3	ZnTPP	Ascorbic acid	H_2O	LBS [b]–Nonion [c]
4	ZnTPP	EDTA	H_2O	LBS [b]
5	ZnTPP	Ascorbic acid	Propan-2-ol	LBS [b]–Nonion [c]

[a] Commercial grade soluble in water. [b] Sodium laurylbenzenesulphonate. [c] Polyoxyethylene octylphenyl ether.

Reduction of the system (run 3) proceeds equally both in the case of an aerated open tube and in a degassed sealed tube. Additionally, a control experiment indicates that (2a) was not observed in the dark under the conditions similar to those of run 3.

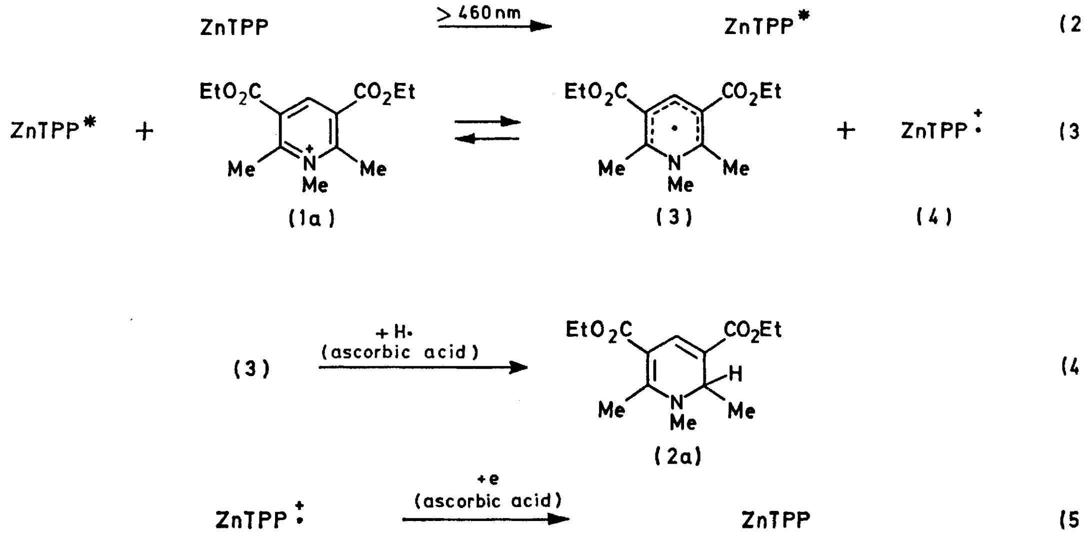
Apparently, photoreduction is initiated by excitation of ZnTPP which is the only light absorbing species (>460 nm). Excited porphyrin, ZnTPP*, may transfer its electron to the reducible pyridinium ion, to give the pyridine radical (3) and a radical cation $ZnTPP^{+\cdot}$ (4). The formation of $ZnTPP^{+\cdot}$ is established by e.s.r. spectroscopy,[2c] and back transfer of an electron to (4) is suppressed by formation of an anionic micelle system by addition of sodium laurylbenzenesulphonate; [2d] otherwise step (3) is rapidly reversible.

Another possible product, the 1,4-dihydropyridine, was not detected. This is probably because the 1,2-dihydro isomer (2a) is more thermally stable than the 1,4-isomer judging from the fact that 1,4-dihydro isomer is irreversibly converted into (2a).[7] In fact, direct photoreduction of (1a) to (2a) by u.v. light was reported to proceed without formation of the 1,4-dihydro isomer.[8]

Fluorescence of ZnTPP was observed under these reaction conditions, its emission maximum being centred at 599 nm. The fluorescence was quenched by (1a) with a quenching constant of 11.6 l mol^{-1}, suggesting that excited ZnTPP* is quenched *via* electron transfer to (1a), because simple energy transfer from ZnTPP* to (1a) is impossible on account of the fact that excited energy of ZnTPP* (whether singlet or triplet) is much lower than that of (1a), *i.e.*, since this transfer would be endothermic. Also, it is a good electron acceptor.[7] Therefore, the quenching study supports the above mechanism.

It is implied that the photoreduction profoundly depends on the electron acceptability of the pyridinium ions. No reduction occurs with (1b), which is probably attributable to its weaker ability as an electron acceptor.

Photoreduction in micelle systems similar to that for (1a) was tried in the other cases such as sodium indigosulphonate, phenanthrenequinone, *o*-phenanthroline (known as an inhibitor of the Hill reaction), sodium *m*-nitrobenzenesulphonate, α-nitronaphthalene, picric acid, *p*-nitrophenol, and 2,4-dinitrophenol. In some cases, photodecomposition occurred, but the photoproducts could not be isolated. The photoconversions of some substrates are as follows: *o*-phenanthroline, 44.8% for 5 h irradiation; *p*-nitrophenol, 72% for 4 h; 2,4-dinitrophenol, 56% for 3 h.



EXPERIMENTAL

Materials.— 1,2,6-Trimethyl-3,5-bisethoxycarbonylpyridinium perchlorate (1a) was prepared by quaternization of 2,6-dimethyl-3,5-bisethoxycarbonylpyridine with dimethyl sulphate followed by addition of a saturated sodium perchlorate solution, m.p. 109—109.5 °C (from ethanol).[8] 1-Methyl-3-carbamoylpyridinium perchlorate (1b) was similarly prepared by the reaction of nicotinamide with dimethyl sulphate followed by addition of a saturated $NaClO_4$ solution. 1,2,6-Trimethyl-3,5-bisethoxycarbonyl-1,2-dihydropyridine (2a) was prepared by the reduction of (1a) with sodium borohydride,[8] $\delta(CCl_4)$ 1.09 (3 H, d, CH_3), 1.30 (6 H, t, 2 × OCH_2CH_3), 2.49 (3 H, s, CH_3), 3.20 (3 H, s, NCH_3), 4.33 (1 H, q, CH), 4.12 (2 H, q, OCH_2), 4.14 (2 H, q, OCH_2), and 7.49 (1 H, s, vinyl H). Zinc(II) tetraphenylporphyrin was synthesised according to Treibs,[9] $\lambda_{max.}$ (benzene) 550 and 589 nm; $\delta(CDCl_3)$ 2.0 (2 H, s, NH), 7.65 (12 H, m, *m*- and *p*-H), 8.08 (8 H, m, *o*-H), and 8.72 (8 H, s, β-H). Ascorbic acid was commercial first grade, and sodium laurylbenzenesulphonate and polyoxyethylene octylphenyl ether were purchased from Nippon Oils and Fats and used without further purification.

Liquid Chromatography.—High pressure liquid chromatography was carried out on a Yanagimoto high pressure liquid chromatograph, model L-1030, employing a Yanapak DMS column (30 cm) with a 254 nm spectroscopic detector using 70% aqueous methanol at a pressure of 30 kg cm^{-2}.

Light Source.—A 150 W halogen lamp (Iwasaki Electrics) was used as the light source. The light was passed through a Corning colour filter to cut off wavelengths <460 nm.

Irradiation of 1,2,6-*Trimethyl*-3,5-*bisethoxycarbonylpyridinium Perchlorate* (1a) *in a Micelle System*.—ZnTPP (1×10^{-3}M) suspended in neat polyoxyethylene octylphenyl ether (0.67% v/v) was diluted with water containing ascorbic acid (1×10^{-2}M). Pyridinium ion (1a) (4×10^{-3}M) and sodium laurylbenzenesulphonate (0.005M) were diluted with this aqueous ZnTPP solution. The mixture was irradiated for 4 h and analysed by liquid chromatography, which indicated the formation of (2a) (*ca.* 1%) (R_F 14 min) by comparison with an authentic specimen. The structure of (2a) was also identified by t.l.c. using benzene–ethyl acetate (33 : 7 v/v), R_F 0.41.

Fluorescence.—Fluorescence spectra were measured by a Hitachi fluorescence spectrophotometer, model MPF-4A. The quenching study of fluorescence of ZnTPP was carried out by changing the concentration of (1a) as quencher between 0 and 6×10^{-3}M, using an aqueous micelle solution of ZnTPP (8.3×10^{-5}M) excited by light of wavelength 548 nm.

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